

Type	Hits	Search Text	DBs	Time Stamp
1 BRS	18487	(copper near3 zinc) and (lopatin or nickel or king)	USPAT; US-PGPUB	2003/03/31 14:52
2 BRS	5498	((copper near3 zinc) and (lopatin or nickel or king)) and alloy	USPAT; US-PGPUB	2003/03/31 14:52
3 BRS	1017	((((copper near3 zinc) and (lopatin or nickel or king)) and alloy) and (electroplating or electroplated))	USPAT; US-PGPUB	2003/03/31 14:53
4 BRS	136	((((copper near3 zinc) and (lopatin or nickel or king)) and alloy) and (electroplating or electroplated)) and semiconductor and solution	USPAT; US-PGPUB	2003/03/31 14:54
5 BRS	2	((((copper near3 zinc) and (lopatin or nickel or king)) and alloy) and (electroplating or electroplated)) and semiconductor and solution) and (advanced adj micro)	USPAT; US-PGPUB	2003/03/31 14:55
6 BRS	134	((((copper near3 zinc) and (lopatin or nickel or king)) and alloy) and (electroplating or electroplated)) and semiconductor and solution) not ((((copper near3 zinc) and (lopatin or nickel or king)) and alloy) and (electroplating or electroplated)) and semiconductor and solution) and (advanced adj micro)	USPAT; US-PGPUB	2003/03/31 14:55

L Number	Hits	Search Text	DB	Time stamp
17	887	(copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)	USPAT; US-PGPUB	2003/04/01 11:09
18	493	((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)	USPAT; US-PGPUB	2003/04/01 10:33
20	471	((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) and @ad<=20020226	USPAT; US-PGPUB	2003/04/01 11:39
22	22	((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) not (((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) and @ad<=20020226)	USPAT; US-PGPUB	2003/04/01 11:08
23	11	((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) not (((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) and @ad<=20020226)) and (pct or wo)	USPAT; US-PGPUB	2003/04/01 11:08
24	6	(copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)	EPO; JPO; DERWENT; IBM TDB	2003/04/01 11:56
26	202	(electroplating or electroplated) and 438/\$.ccls.	EPO; JPO; DERWENT; IBM TDB	2003/04/01 11:56
27	29	((electroplating or electroplated) and 438/\$.ccls.) and copper	EPO; JPO; DERWENT; IBM TDB	2003/04/01 11:54
28	2892	(electroplating or electroplated) and 438/\$.ccls.	USPAT; US-PGPUB	2003/04/01 12:13
29	2184	((electroplating or electroplated) and 438/\$.ccls.) and copper	USPAT; US-PGPUB	2003/04/01 11:57
30	1495	((electroplating or electroplated) and 438/\$.ccls.) and copper) and via	USPAT; US-PGPUB	2003/04/01 11:58
31	505	((((electroplating or electroplated) and 438/\$.ccls.) and copper) and via) and (copper with seed)	USPAT; US-PGPUB	2003/04/01 12:15
32	387	(electroplating or electroplated) and 205/82,170,115,182,183.ccls.	USPAT; US-PGPUB	2003/04/01 12:13
34	313	((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and copper	USPAT; US-PGPUB	2003/04/01 12:14
36	309	((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and copper) not (((((electroplating or electroplated) and 438/\$.ccls.) and copper) and via) and (copper with seed))	USPAT; US-PGPUB	2003/04/01 13:01
33	45	((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and (copper with seed)	USPAT; US-PGPUB	2003/04/01 13:02
37	10	((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and (copper with seed)) and zinc	USPAT; US-PGPUB	2003/04/01 13:05
38	110	((((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and copper) not (((((electroplating or electroplated) and 438/\$.ccls.) and copper) and via) and (copper with seed))) and zinc	USPAT; US-PGPUB	2003/04/01 14:08
39	405	annealing with oxygen with concentration	USPAT; US-PGPUB	2003/04/01 14:16

40	1	(annealing with oxygen with concentration) same (copper with zinc)	USPAT; US-PGPUB	2003/04/01 14:18
41	1		USPAT	2003/04/01 14:11
42	1		USPAT	2003/04/01 14:11
43	1		USPAT	2003/04/01 14:12
44	1		USPAT	2003/04/01 14:12
45	1		USPAT	2003/04/01 14:14
46	1		USPAT	2003/04/01 14:14
47	1		USPAT	2003/04/01 14:14
48	0		USPAT	2003/04/01 14:14
49	0		USPAT	2003/04/01 14:14
50	0		USPAT	2003/04/01 14:14
51	1	("20020074234").PN.	USPAT; US-PGPUB	2003/04/01 14:15
52	87	annealing with oxygen with concentration	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:22
53	0	(annealing with oxygen with concentration) same (copper with zinc)	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:16
54	3	(annealing with oxygen with concentration) same (copper)	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:16
55	5	(annealing with oxygen with concentration) same (copper)	USPAT; US-PGPUB	2003/04/01 14:22
56	2	(annealing with oxygen with concentration) same (copper with alloy)	USPAT;	2003/04/01 14:22
57	97	annealing with copper with zinc	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:26
58	5	(annealing with copper with zinc) and oxygen	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:26
59	63	annealing with copper with zinc	USPAT; US-PGPUB	2003/04/01 14:26
60	26	(annealing with copper with zinc) and oxygen	USPAT; US-PGPUB	2003/04/01 14:26

DOCUMENT-IDENTIFIER: US 20020008034 A1

TITLE: Apparatus and method for electrochemically depositing metal on a semiconductor workpiece

----- KWIC -----

[0040] FIG. 4C is a graph of sheet resistance change with annealing temperature for copper films deposited from a bath solution with and without ammonium sulfate.

[0067] Although the embodiment of the process disclosed herein is described in connection with copper metallization, it is understood that the basic principle of the enhancement of an ultra-thin seed layer prior to the bulk deposition thereof can be applied to other metals or alloys that are capable of being electroplated. Such metals include iron, nickel, cobalt, zinc, copper-zinc, nickel-iron, cobalt-iron, etc.

[0086] Experimental results indicate that addition of ammonium sulfate significantly reduces the resistivity of the plating bath solution and, as such, the deposited film. The sheet resistance obtained for different amounts of ammonium sulfate are compared in the graph FIG. 4C. As can be seen, the highest sheet resistance, either with or without annealing at high temperatures, was obtained in the bath containing no ammonium sulfate. If ammonium hydroxide was used to adjust pH in which a trace amount of ammonium sulfate is introduced to the bath, the sheet resistance was reduced from 76 to 23. As the concentration of ammonium sulfate increased from 0.1 M to 0.5 M, the sheet resistance continuously decreased in a corresponding manner.

[0094] With reference again to the specific seed layer enhanced aspects of

the present invention, the enhanced seed layer of FIG. 2C is suitable for subsequent electrochemical copper deposition. This subsequent copper deposition may take place in an alkaline bath within the apparatus employed to enhance the seed layer. This may be followed by a low-temperature annealing process that assists in lowering the resistivity of the deposited copper. Such a low-temperature annealing process suitably takes place at a temperature below about the 250 degrees Celsius and, more suitably, below about 100 degrees Celsius. When a low-K dielectric material is employed to isolate the copper structures, the upper annealing temperature limit should be chosen to be below the degradation temperature of the dielectric material.

[0181] FIG. 22 illustrates a further embodiment of a processing tool in which an RTP station 1635, located in portion 1630, that includes at least one thermal reactor, may be integrated in a tool set. Unlike the embodiment of FIG. 21, in this embodiment, at least one thermal reactor is serviced by a dedicated robotic mechanism 1640. The dedicated robotic mechanism 1640 accepts workpieces that are transferred to it by the robotic transfer mechanisms 1620. Transfer may take place through an intermediate staging door/area 1645. As such, it becomes possible to hygienically separate the RTP portion 1630 of the processing tool from other portions of the tool. Additionally, using such a construction, the illustrated annealing station may be implemented as a separate module that is attached to upgrade an existing tool set. It will be recognized that other types of processing stations may be located in portion 1630 in addition to or instead of RTP station 1635.

US-PAT-NO:

6290833

DOCUMENT-IDENTIFIER: US 6290833 B1

TITLE:

Method for electrolytically depositing copper on a semiconductor workpiece

----- KWIC -----

This invention employs a novel approach to the copper metallization of a workpiece, such as a semiconductor workpiece. In accordance with the invention, an alkaline electrolytic copper bath is used to electroplate copper onto a seed layer, electroplate copper directly onto a barrier layer material, or enhance an ultra-thin copper seed layer which has been deposited on the barrier layer using a deposition process such as PVD. The resulting copper layer provides an excellent conformal copper coating that fills trenches, vias, and other microstructures in the workpiece. When used for seed layer enhancement, the resulting copper seed layer provide an excellent conformal copper coating that allows the microstructures to be filled with a copper layer having good uniformity using electrochemical deposition techniques. Further, copper layers that are electroplated in the disclosed manner exhibit low sheet resistance and are readily annealed at low temperatures.

This invention employs a novel approach to the copper metallization of a workpiece, such as a semiconductor workpiece. In accordance with the invention, an alkaline electrolytic copper bath is used to electroplate copper onto a seed layer, electroplate copper directly onto a barrier layer material, or enhance an ultra-thin copper seed layer which has been deposited on the barrier layer using a deposition process such as PVD. The resulting copper layer provides an excellent conformal copper coating that fills trenches, vias,

and other microstructures in the workpiece. When used for seed layer enhancement, the resulting copper seed layer provide an excellent conformal copper coating that allows the microstructures to be filled with a copper layer having good uniformity using electrochemical deposition techniques. Further, copper layers that are electroplated in the disclosed manner exhibit low sheet resistance and are readily annealed at low temperatures.

Various plating bath compositions suitable for blanket plating, fill-plating of recessed micro-structures, and seed layer enhancement plating are also set forth. A preferred solution for electroplating copper for seed layer enhancement comprises copper sulfate, boric acid, and a complexing agent. The complexing agent is preferably selected from the group consisting of ED, EDTA, and a polycarboxylic acid, such as citric acid. This solution is also suitable for blanket plating and fill-plating of recessed micro-structures.

The use of an ultra-thin seed layer 15 generally introduces its own set of problems. One of the most significant of these problems is the fact that such ultra-thin layers do not generally coat the barrier layer 10 in a uniform manner. Rather, voids or non-continuous seed layer regions on the sidewalls, such as at 20, are often present in an ultra-thin seed layer 15 thereby resulting in the inability to properly apply a subsequent electrochemically deposited copper layer in the regions 20. Further, ultra-thin seed layers tend to include spikes, such as at 21, that impact the uniformity of the subsequent electrolytically deposited metal layer. Such spikes 21 result in high potential regions at which the copper deposits at a higher rate than at other, more level regions. As such, the seed layer 15 is not fully suitable for the traditional electroplating techniques typically used after application of a seed layer.

Although the embodiment of the process disclosed herein is described in connection with copper metallization, it is understood that the basic principle of the enhancement of an ultra-thin seed layer prior to the bulk deposition thereof can be applied to other metals or alloys that are capable of being electroplated. Such metals include iron, nickel, cobalt, zinc, copper-zinc,

nickel-iron, cobalt-iron, etc.

A schematic representation of an apparatus 25 suitable for enhancing the ultra-thin copper seed layer is illustrated in FIG. 3. It will be recognized that this apparatus is also suitable for applying a blanket plating layer and/or full-fill plating of recessed micro-structures. As shown, a semiconductor workpiece, such as a semiconductor wafer 30, is positioned face down in a bath 35 of **electroplating** solution. One or more contacts 40 are provided to connect the wafer 30 to a plating power supply 45 as a cathode of an **electroplating** cell. An anode 50 is disposed in the bath 35 and is connected to the plating power supply 45. Preferably, a diffuser 55 is disposed between the anode 50 and the wafer/cathode 30. The wafer 30 may be rotated about axis 60 during the enhancement process. Anode 50 may be provided with a dielectric shield 65 at a backside thereof which faces an incoming stream of plating bath fluid.

A further advantage of using a polycarboxylic acid, such as citric acid, stems from the fact that the magnitude of the voltage potential at which the copper is plated is greater than the magnitude of the voltage potential at which the copper is plated in a bath containing EDTA. This is illustrated in FIGS. 4A and 4B where FIG. 4A is a current-potential graph for a citric acid bath, and FIG. 4B is a current-potential graph for an EDTA bath. **Electroplating** takes place at the voltage where the corresponding current increases abruptly. This plating voltage is referred to as the deposition potential, which is approximately -1.25 volts as shown in FIG. 4A for a bath employing citric acid as the complexing agent, and is approximately -1.0 volts as shown in FIG. 4B for a bath employing EDTA as the complexing agent. The current peaks (7070' for the a bath containing a citric acid, and 72, 72' for the bath containing the EDTA) are the limiting currents which are mainly determined by mass transfer and the concentration of copper ions in the plating solutions. As illustrated, the magnitude of the current and the particular plating potential is slightly dependent on the substrate material. The different substrate results are illustrated in FIGS. 4A and 4B, where 70 and 72 are the curves for a copper substrate material, and 70' and 72' are curves for a copper substrate material comprised of copper with a copper oxide coating.

It is noted that additional peaks occur on oxidized copper in the same electrolytes. These peaks are related to the electrochemical reduction of copper oxide to metallic copper before the alkaline electrochemical copper deposition.

As can be seen from the results in Table 1 above, seed layer enhancement in accordance with the disclosed process provides excellent uniformity (6 to 7%) compared to that without seed layer enhancement (46%). This is consistent with observations during visual examination of the wafer after 1.5 micron **electroplated copper** had been deposited. Such visual examination of the wafer revealed the presence of defects at wafer electrode contact points on the wafer without seed layer enhancement.

providing a first electroplating bath including copper sulfate as a source of metal ions as a principal metal species to be deposited during subsequent electroplating, ammonium sulfate, a complexing agent, and ethylene glycol;

exposing at least one surface of the workpiece to the first electroplating bath;

providing electroplating power between the at least one surface of the workpiece and an anode disposed in electrical contact with the first electroplating bath to electroplate copper onto the at least one surface of the workpiece in an electrolytic first deposition process; and

3. The process of claim 1, wherein the first electroplating bath comprises an alkaline bath.

providing a first electroplating bath including copper sulfate as a source of metal ions as a principal metal species to be deposited during subsequent electroplating, a complexing agent, and ethylene glycol;

exposing at least one surface of the workpiece to the first electroplating

bath;

providing electroplating power between the at least one surface of the workpiece and an anode disposed in electrical contact with the first electroplating bath to electroplate copper onto the at least one surface of the workpiece in an electrolytic first deposition process at a first deposition rate; and

providing a first electroplating bath including copper sulfate as a source of principal metal species to be deposited during subsequent electroplating, ethylene glycol, a metal ion complexing agent, and an alkaline agent in an amount to adjust the pH of the first electroplating bath to a pH of at least 9.0;

exposing the least one surface of the workpiece including the barrier layer to the first electroplating bath;

providing electroplating power between the at least one surface of the workpiece and an anode disposed in electrical contact with the first electroplating bath to electroplate copper directly onto the barrier layer of the workpiece in an electrolytic first deposition process; and

providing a first electroplating bath including copper sulfate as a source of metal ions as a principal metal species to be deposited during subsequent electroplating, a complexing agent, ethylene glycol, and an alkaline agent in an amount sufficient to raise the pH of the bath to at least 9.0;

exposing at least one surface of the workpiece to the first electroplating bath;

providing electroplating power between the at least one surface of the workpiece and an anode disposed in electrical contact with the first electroplating bath to electroplate copper onto the at least one surface of the

workpiece in an electrolytic first deposition process; and

21. A **copper electropolating** solution comprising copper sulfate as a source of copper ions at a level so as to be the principal metal species, ammonium sulfate, and ethylene glycol at a level of greater than 0 to 1.0 Molar, the solution being formulated so as to be suitable for electrodeposition of copper onto a microelectronic workpiece.

205/182

205/170

US-PAT-NO:

6313064

DOCUMENT-IDENTIFIER:

US 6313064 B1

TITLE:

Alloy having antibacterial effect and sterilizing effect

----- KWIC -----

In order to oxidize titanium, silicon, or zinc for the copper alloy of the present invention, heat treatment may be conducted in the air or in vacuum in such a manner that the real temperature of the copper alloy is set up to 200-800.degree. C. by a heating furnace such as an electrical furnace or a gas furnace, corona discharge, glow discharge, laser rays, plasma, or infrared rays. Since these elements have far more intense affinity with oxygen (standard free energy for the production of oxides) than copper, they can be preferentially oxidized. Oxygen is diffused in the copper alloy, and thus the alloy can be industrially produced in such a manner that the amount or size of produced oxides, the depth of the oxidized layer, and the like are controlled by combining heating atmosphere (oxygen partial pressure), heating temperature and heating time appropriately. If the heating temperature is lower than 200.degree. C., the speed of the preferential oxidization of Ti, Zn and Si becomes slow so that the time for the oxidization is prolonged. If the heating temperature is over 800.degree. C., copper itself is intensely oxidized so that the loss of heating energy becomes large. It also becomes difficult that the oxidization of Ti, Zn and Si is controlled. Accordingly, the heating temperature is set up in the manner that the real temperature of the copper alloy is 200-800.degree. C.

L Number	Hits	Search Text	DB	Time stamp
17	887	((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench))	USPAT; US-PPGPUB	2003/04/01 11:09
18	493	((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)	USPAT; US-PPGPUB	2003/04/01 10:33
20	471	((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) and @ad<=20020226	USPAT; US-PPGPUB	2003/04/01 11:39
22	22	((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) not (((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) and @ad<=20020226)	USPAT; US-PPGPUB	2003/04/01 11:08
23	11	((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) not (((copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)) and (annealing or baking or heating)) and @ad<=20020226)) and (pct or wo)	USPAT; US-PPGPUB	2003/04/01 11:08
24	6	(copper near3 zinc) and (electroplating or electroplated) and (via or hole or opening or recess or trench)	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 11:56
26	202	(electroplating or electroplated) and 438/\$.ccls.	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 11:56
27	29	((electroplating or electroplated) and 438/\$.ccls.) and copper	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 11:54
28	2892	(electroplating or electroplated) and 438/\$.ccls.	USPAT; US-PPGPUB	2003/04/01 12:13
29	2184	((electroplating or electroplated) and 438/\$.ccls.) and copper	USPAT; US-PPGPUB	2003/04/01 11:57
30	1495	((electroplating or electroplated) and 438/\$.ccls.) and copper) and via	USPAT; US-PPGPUB	2003/04/01 11:58
31	505	(((electroplating or electroplated) and 438/\$.ccls.) and copper) and via) and (copper with seed)	USPAT; US-PPGPUB	2003/04/01 12:15
32	387	(electroplating or electroplated) and 205/82,170,115,182,183.ccls.	USPAT; US-PPGPUB	2003/04/01 12:13
34	313	((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and copper	USPAT; US-PPGPUB	2003/04/01 12:14
36	309	((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and copper) not (((electroplating or electroplated) and 438/\$.ccls.) and copper) and via) and (copper with seed))	USPAT; US-PPGPUB	2003/04/01 13:01
33	45	((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and (copper with seed)	USPAT; US-PPGPUB	2003/04/01 13:02
37	10	((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and (copper with seed)) and zinc	USPAT; US-PPGPUB	2003/04/01 13:05
38	110	(((electroplating or electroplated) and 205/82,170,115,182,183.ccls.) and copper) not (((electroplating or electroplated) and 438/\$.ccls.) and copper) and via) and (copper with seed))) and zinc annealing with oxygen with concentration	USPAT; US-PPGPUB	2003/04/01 14:08
39	405		USPAT; US-PPGPUB	2003/04/01 14:16

40	1	(annealing with oxygen with concentration) same (copper with zinc)	USPAT; US-PPGPUB	2003/04/01 14:18
41	1		USPAT	2003/04/01 14:11
42	1		USPAT	2003/04/01 14:11
43	1		USPAT	2003/04/01 14:12
44	1		USPAT	2003/04/01 14:12
45	1		USPAT	2003/04/01 14:14
46	1		USPAT	2003/04/01 14:14
47	1		USPAT	2003/04/01 14:14
48	0		USPAT	2003/04/01 14:14
49	0		USPAT	2003/04/01 14:14
50	0		USPAT	2003/04/01 14:14
51	1	("20020074234").PN.	USPAT; US-PPGPUB	2003/04/01 14:15
52	87	annealing with oxygen with concentration	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:22
53	0	(annealing with oxygen with concentration) same (copper with zinc)	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:16
54	3	(annealing with oxygen with concentration) same (copper)	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:16
55	5	(annealing with oxygen with concentration) same (copper)	USPAT; US-PPGPUB	2003/04/01 14:22
56	2	(annealing with oxygen with concentration) same (copper with alloy)	USPAT; US-PPGPUB	2003/04/01 14:22
57	97	annealing with copper with zinc	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:26
58	5	(annealing with copper with zinc) and oxygen	EPO; JPO; DERWENT; IBM_TDB	2003/04/01 14:26
59	63	annealing with copper with zinc	USPAT; US-PPGPUB	2003/04/01 14:26
60	26	(annealing with copper with zinc) and oxygen	USPAT; US-PPGPUB	2003/04/01 14:47
61	10	(affinity with oxygen) same (copper with zinc)	USPAT; US-PPGPUB	2003/04/01 14:51

DOCUMENT-IDENTIFIER: US 20020050628 A1

TITLE:

Metalization structures for microelectronic applications and process for forming the structures

----- KWIC -----

[0009] Another problem is the propensity of copper to oxidize rapidly when immersed in aqueous solutions or when exposed to an oxygen-containing atmosphere. Oxidized surfaces of the copper are rendered non-conductive and thereby limit the current carrying capability of a given conductor path when compared to a similarly dimensioned non-oxidized copper path.

[0017] FIG. 2 is a chart showing the relationship between the resistivity of a copper-zinc alloy layer as a function of the annealing temperature.

[0034] Notwithstanding the particular deposition technique used to deposit the layer, the present inventors have found that the resistivity of the copper-zinc alloy layer 40 may be reduced using a low-temperature annealing process. FIG. 2 is a chart showing the relationship between the resistivity of a copper-zinc alloy layer as a function of the annealing temperature for a number of samples in which the copper-zinc alloy was sputter deposited on the dielectric material. The sputtering was done at 2.5 kW (0.5 k volt.times.5 amps) with a base pressure of 10.<sup>sup.7</sup> Torr and an argon pressure of 5 mtorr for 10 minutes. The annealing took place at the given temperatures for a time period of 30 minutes. The sputter target had a zinc content of 5 atomic percent.

[0035] As illustrated, annealing under the foregoing conditions generally improved the resistivity of the copper-alloy layer when compared to the

resistivity of the layer as originally deposited. The results show a general decrease in resistivity with increasing annealing temperature. However, the resistivity was not significantly enhanced with increasing annealing temperatures above about 350.degree. C.-400.degree. C. As such, given the diminishing resistivity enhancement provided above such temperatures, it has been found to be preferable to anneal the **copper-zinc** alloy layer at an annealing temperature that is at or below this temperature range, thereby increasing the available thermal budget of the microelectronic workpiece (e.g., a semiconductor wafer). The annealing process may take place at an even lower temperature when one or more of the layers of the overall microelectronic workpiece degrade or are otherwise stressed when subject to high annealing temperatures. For example, many low-K dielectric materials begin to degrade at temperatures above about 250.degree. C.-350.degree. C. As such, annealing must take place below such temperatures.

PAT-NO: JP403138342A  
DOCUMENT-IDENTIFIER: JP 03138342 A  
TITLE: PRODUCTION OF COPPER ALLOY  
PUBN-DATE: June 12, 1991

INVENTOR- INFORMATION:  
NAME  
TANIGAWA, TORU  
MORIKAWA, TAKAFUMI  
FUKUDA, MASUO

ASSIGNEE- INFORMATION:  
NAME  
FURUKAWA ELECTRIC CO LTD: THE  
COUNTRY  
N/A

APPL-NO: JP01273022  
APPL-DATE: October 20, 1989  
INT-CL (IPC): C22F001/08, C22C009/00  
US-CL-CURRENT: 148/684

ABSTRACT:

PURPOSE: To produce a copper alloy having superior surface quality by carrying out at least the final annealing of a copper alloy containing easily oxidizable metal in a nonoxidizing or reducing atmosphere of specific oxygen concentration.

CONSTITUTION: One or more elements among Cr, Si, Ti, and Al are added and dissolved into electrolytic copper, and the resulting mixture is subjected to hot working, cold working, and annealing, by which a precipitation-type copper alloy is obtained. In a method for producing the above copper alloy containing easily oxidizable metal, at least the final annealing is performed in a nonoxidizing atmosphere of  $N<SB>2</SB>$  or Ar or in a reducing atmosphere of  $H<SB>2</SB>$ ,  $H<SB>2</SB>+N<SB>2</SB>+Ar$ , etc. Further, oxygen concentration in the above atmosphere is regulated to  $\leq 0.1\text{ppm}$ . By this method, the precipitation-type high-efficiency copper alloy containing easily oxidizable metal can be obtained without deteriorating surface quality.

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⑨日本国特許庁(JP) ⑩特許出願公開  
⑪公開特許公報(A) 平3-138342

⑫Int. Cl.<sup>3</sup>  
C 22 F 1/08  
C 22 C 9/00

識別記号 庁内整理番号  
S 8015-4K  
8015-4K

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⑭発明の名称 銅合金の製造方法

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明細書

1. 発明の名称

銅合金の製造方法

2. 特許請求の範囲

(1) 易酸化性金属を含有する銅合金の製造において、少なくとも最終の焼純の雰囲気を非酸化性又は還元性とし、且つその雰囲気の酸素濃度を0.1ppm以下とすることを特徴とする銅合金の製造方法。

(2) 銅合金に含有される易酸化性金属がCr, Si, Ti, Alから選ばれる1種又は2種以上である請求項(1)記載の銅合金の製造方法。

(3) 非酸化性雰囲気としてはN<sub>2</sub>又はArを、還元性雰囲気としてはH<sub>2</sub>, H<sub>2</sub>+N<sub>2</sub>又はH<sub>2</sub>+Arを用いる請求項(1)又は(2)記載の銅合金の製造方法。

3. 発明の詳細な説明

【産業上の利用分野】

本発明は銅合金の線、棒、条、板等の製造方

法に関し、特に銅合金のメッキ性や半田付け性等を向上したものである。

【従来の技術】

銅合金を製造するには一般に、先ず電気銅と合金添加成分を溶解して円筒形のビレットや直方形のスラブに鋳造する。そしてこの鋳塊を熱間で押し出しや圧延加工を施した後、冷間加工と焼純とを繰り返して所望の形状や機械的特性を有した製品を得るという方法である。

このような製造工程中、焼純工程では銅合金の酸化変色を防止するために、非酸化性のN<sub>2</sub>雰囲気や還元性のH<sub>2</sub>やCOを含んだ雰囲気が利用されている。

【発明が解決しようとする課題】

近年エレクトロニクス用を中心に銅合金の高性能化が求められており、従来の固溶型を中心とする合金に代わって析出型の合金が開発されている。

そしてこのような析出型の合金には易酸化性金属であるCr, Si, Ti等が使用されているが、

銅の変色を防止するための従来の焼純条件で製造したこれら合金はメッキ性や半田付け性等の点で表面品質上問題があった。

〔課題を解決するための手段〕

本発明はこれに燃み種々検討の結果、上記問題を解消した銅合金の製造方法を提供するものである。

即ち本発明は、易酸化性金属を含有する銅合金の製造において、少なくとも最終の焼純の雰囲気を非酸化性又は還元性とし、且つその雰囲気の酸素濃度を0.1ppm以下とすることを特徴とするものである。そしてこのような銅合金に含有される易酸化性金属としてはCr, Si, Ti, Alから選ばれる1種又は2種以上があり、さらに非酸化性雰囲気としてはN<sub>2</sub>又はAr、還元性雰囲気としてはH<sub>2</sub>, H<sub>2</sub>+N<sub>2</sub>又はH<sub>2</sub>+Arを用いるのが有効である。

〔作用〕

前記のような不具合は従来合金でも表面問題として顕在化していたが、その原因是表面の酸

とが肝要である。

しかして上記のように易酸化性金属を含有する銅合金の最終焼純での雰囲気の酸素濃度を0.1ppm以下としたのは、0.1ppmを超えると銅自身は酸化しないが上記の易酸化性金属は酸化してしまうからである。なお酸素濃度が0.1ppm以下であればそれまで存在していた酸化物の一部が分解するのでより効果的である。

〔実施例〕

次に本発明を実施例によってさらに詳細に説明する。

〔実施例1〕

Cu-Cr-Si合金(0.3%Cr-0.1%Si)をAr雰囲気中で溶解後、200°C×500°C×20°Cの鋳塊とした。その後この鋳塊を8mm<sup>3</sup>の厚さに熱間加工後表面を研削し、しかし後冷間圧延と焼純とを繰り返して0.4mm<sup>3</sup>の条となし、さらにこれを焼純後湿式バフを用いて表面を研磨し、表面層を除去した。そしてその後冷間圧延を行い0.2mm<sup>3</sup>の条とした。

化や異物の付着によるところが多く、易酸化性金属の酸化の例は少なかった。

さらに酸化を防止するのに酸素分圧を下げることは熱力学的には自明のことであるが、易酸化性金属を含有する銅合金について工業的に発現した例はかつてみない。

即ち銅合金の工業的な製造において用いられている焼純炉は、一般に連続炉とバッチ炉に大別されるが、前者ではCOやH<sub>2</sub>を含有する燃焼ガスが、後者ではNH<sub>3</sub>分解ガスやN<sub>2</sub>+H<sub>2</sub>ガスが利用されている。そしていずれも還元性ガスであり、銅の変色防止を主眼としたものであって、このような還元性ガスの効果を期待できない易酸化性元素の酸化に重要なO<sub>2</sub>や高温での反応平衡でO<sub>2</sub>を生ずるH<sub>2</sub>OやCO<sub>2</sub>について考慮することはなかった。

本発明にあってはこのような雰囲気成分を考慮することは重要であり、特に精製の困難な燃焼ガスは使用できず、またその他のガスについてもO<sub>2</sub>やH<sub>2</sub>Oについて十分な注意を払うこと

この条を用いて、400°Cの温度及び第1表に示した雰囲気中でそれぞれ30min焼純した後、ロジン系フワックス(田村化研製MH820V)を用いて230°Cの共晶半田に3秒間浸漬して半田濡れ性を評価してそれらの結果を第1表に併記した。

製造法	No	雰囲気	O <sub>2</sub> 濃度(ppm)	表面変色	半田付後外観
本発明法	1	N <sub>2</sub> +20%H <sub>2</sub>	0.02	なし	良(>95%)
"	2	"	0.08	"	良(>95%)
"	3	N <sub>2</sub>	0.03	"	良(>95%)
比較法	4	"	0.07	"	良(>95%)
"	5	Ar	0.06	"	良(>95%)
比較法	6	N <sub>2</sub> +20%H <sub>2</sub>	0.3	"	やや劣(85%)
"	7	"	0.8	"	劣(80%)
"	8	"	1.5	"	劣(70%)
"	9	N <sub>2</sub>	0.6	"	劣(85%)
"	10	"	1.8	あり	劣(60%)

() 内は濡れ面積の割合

第1表から、焼純時の酸素濃度が0.1ppm以下の本発明法No.1～No.5はいずれも特性上の問題はないが、酸素量が0.1ppmを超える比較法No.6～No.10は還元性及び非酸化性雰囲気を問わず半田濡れ性が低下することが明らかである。さらに銅の酸化を伴う非酸化性雰囲気No.10では半田濡れ性は一層低下することが判る。

## &lt;実施例2&gt;

第2表に示す3種類の銅合金を実施例1と同様に作製した。そしてこれら合金を十分に精製したN<sub>2</sub>-20%H<sub>2</sub>雰囲気中で第2表に示すようにO<sub>2</sub>濃度を変化させて焼純した後、実施例1と同様に半田濡れ性を評価してその結果を第2表に併記した。

製造法	No	O <sub>2</sub> 濃度	Cu-3.1Ni-0.72Si			Cu-1.3Ni-0.27Mn			Cu-5Ni		
			変色	半田濡れ性	変色	半田濡れ性	変色	半田濡れ性	変色	半田濡れ性	変色
本発明法	11	<0.01	なし	良(95%)	なし	良(100%)	なし	良(100%)	なし	良(100%)	なし
"	12	0.03	"	良(95%)	"	良(95%)	"	良(100%)	"	良(100%)	"
"	13	0.07	"	良(95%)	"	良(95%)	"	良(100%)	"	良(100%)	"
比較法	14	0.2	"	不良(85%)	"	不良(85%)	"	良(100%)	"	良(100%)	"
"	15	0.4	"	不良(85%)	"	不良(85%)	"	良(95%)	"	良(95%)	"

() 内は濡れ面積の割合

第2表から明らかなように、Niのみを含有する銅合金はいずれの酸素濃度であっても表面に変色はなく、また半田濡れ性も良好である。一方SiやTiを含む合金では表面変色はないものの、酸素濃度が0.1ppmを超える比較法No.14及びNo.15の半田濡れ性は劣っていることが判る。

## 〔発明の効果〕

このように本発明によれば、易酸化性金属を含む高性能銅合金が表面品質を低下せしめることなく製造でき、工業的価値は極めて大きいものである。

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